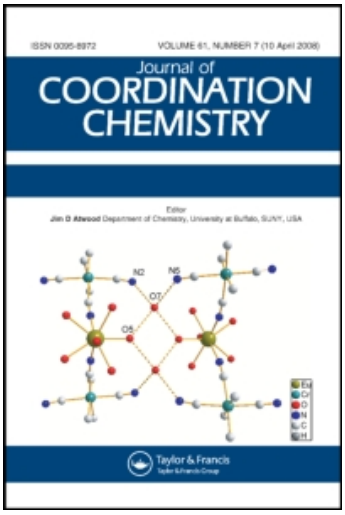
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEX EQUILIBRIA INVOLVING TRIPHENYLTIN(IV) SOME SELECTED AMINO ACIDS AMD NUCLEOTIDES

M. M. Shoukry[a]; M. M. H. Mohamed[a]
[a] Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

To cite this Article Shoukry, M. M. and Mohamed, M. M. H.(1998) 'COMPLEX EQUILIBRIA INVOLVING TRIPHENYLTIN(IV) SOME SELECTED AMINO ACIDS AMD NUCLEOTIDES', Journal of Coordination Chemistry, 43: 2, 217 — 225
To link to this Article: DOI: 10.1080/00958979808022670
URL: http://dx.doi.org/10.1080/00958979808022670

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1998, Vol. 43, pp. 217–225
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

COMPLEX EQUILIBRIA INVOLVING TRIPHENYLTIN(IV) WITH SOME SELECTED AMINO ACIDS AND NUCLEOTIDES

M.M. SHOUKRY* and M.M.H. MOHAMED

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

(Received 9 October 1996; In final form 28 January 1997)

Downloaded At: 15:30 23 January 2011

Complex formation equilibria for triphenyltin(IV) with selected aminoacids and nucleotides having a variety of model functional groups were studied. Stoichiometries and stability constants for the complexes formed were determined by a potentiometric technique, in 75% dioxane-water solution. Amino acids and nucleotides are bound to $Ph_3Sn(IV)$ as monodentates. The effect of the pK_a of the amino acid on the stability constant of its complex species was elucidated. Concentration distributions of the various complex species were evaluated as a function of pH.

Keywords: complex formation, equilibria, triphenyltin(IV), aminoacid, nucleotides

INTRODUCTION

Organotin compounds have attracted considerable attention because of their significant biological activity. The first work on the biological properties of triphenyltin(IV) compounds was carried out in the early 1950s by van der Kerk and Luijten, who discovered the high fungicidal activity of triphenyltin(IV) compounds [1]. The first organotin compounds to reach commercialisation were triphenyltin(IV) acetate and triphenyltin(IV) hydroxide, both of which are widely used [2, 3] to combat a number of fungal diseases in various crops, particularly potato blight, leaf spot on sugar beet and celery, rice blast and coffee leaf rust. A further interesting property [4] of these triphenyltin fungicides is that they function as "antifeedants", in that they deter insects from feeding, and they may also act as insect chemosterilants.

A detailed knowledge of the complex formation ability of triphenyltin(IV) with bioligands such as amino acids and DNA units has confirmed the biological

*Author for correspondence.

significance of this reagent. In continuation of our current studies of organotin(IV) complexes [5-8], the present investigation traces the formation and characteristics of triphenyltin(IV) complexes involving selected amino acids and nucleotides.

EXPERIMENTAL

Materials and Reagents

Triphenyltin(IV) chloride (TPT) was received from Merck Chem. Co. The ligands (L) used were (natural hand of optically active aminoacids) glycine, alanine, proline, valine, β-phenylalanine, *S*-methylcysteine, *iso*-leucine, threonine, serine, methylamine, imidazole, acetic acid, histidine, histamine.2HCl, lysine.HCl, ornithine.HCl, penicillamine, mercaptoethylamine.HCl, mercaptopropionic acid, cysteine, inosine, uracil, thymine, thymidine and adenine. These were supplied by Fluka Chem. Co. Triphenyltin(IV) chloride was converted to the perchlorate by suspending it in dioxane, adding 0.99 equivalents of $AgClO_4$ and stirring over night. The precipitate was filtered off and the resulting final solution was made up in 75% dioxane-water solution. The concentration of TPT was checked potentiometrically. Solutions of methylamine, imidazole and histidine were prepared in the protonated form by dissolving in equimolar HNO_3 solutions. Carbonate-free sodium hydroxide stock solutions were prepared by diluting the contents of BDH concentrated volumetric solution vials. These solutions were systematically checked by titration against potassium hydrogen phthalate. All solutions were prepared in deionized water.

Downloaded At: 15:30 23 January 2011

Procedure and Measuring Techniques

Potentiometric titrations were performed using a Metrohm 686 titroprocessor equipped with a 665 dosimat (Switzerland-Herisaue). The titroprocessor and electrode were calibrated with standard buffer solutions, prepared according to NBS specifications [9]. The titrations were carried out in a purified nitrogen atmosphere using a titration vessel described previously [10]. The temperature was maintained constant by a Colora ultrathermostat; pK_w in 75% dioxane-water solutions was determined as described previously [11]. For this purpose various amounts of standard NaOH solution (in 75% dioxane) were added to a solution containing 0.10 M $NaNO_3$. The value of $-\log[H]$ was calculated from the amount of base added. The product of [OH] and [H] was taken and the mean value obtained in this way for the log concentration product is $\log K_w = 16.21$. This value is in good agreement with that previously determined in 70% dioxane, as $\log K_w = 16.0$ [11].

The following mixtures (A)-(C) were prepared in 75% dioxane-water mixture and titrated potentiometrically with standardized NaOH solution, ~0.1 M.

(A) 40 cm^3 of a solution containing 2.5×10^{-3} M ligand and 0.1 M $NaClO_4$.
(B) 40 cm^3 of a solution containing 2.5×10^{-3} M TPT and 0.1 M $NaClO_4$.
(C) 40 cm^3 of a solution containing 2.5×10^{-3} M TPT, 2.5×10^{-3} M ligand and 0.1 M $NaClO_4$.

The acid dissociation constants of the ligands were determined by titrating mixture (A) of each. The stability constants of the hydroxo complexes [TPT(OH)] were determined by titrating mixture (B). The stability constants of the triphenyltin(IV) complexes were determined by titrating mixture (C).

Equilibrium constants were evaluated from titration data. These are defined by equations (*1*) and (*2*)

$$1(M) + p(L) + q(H) \rightleftarrows (M)_1(L)_p(H)_q \qquad (1)$$

$$\beta_{1pq} = \frac{[(M)_1(L)_p(H)_q]}{[M]^1[L]^p[H]^q} \qquad (2)$$

Here, M, L and H represent organotin(IV), ligand and proton respectively. Calculations were performed using the computer program [12] MINIQUAD-75 loaded on an IBM 486 computer. The model selected gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals, as described elsewhere [12]. The fitted model was tested by comparing the experimental titration data points and the theoretical curve calculated from the values of acid dissociation constant of the ligand and formation constants of the corresponding complexes. The results obtained are listed in Table I. The concentration distribution diagrams were obtained using the program SPECIES [13]

RESULTS AND DISCUSSION

The acid dissociation constants of the ligands have been reported [14]. We redetermined them under the experimental conditions used for determining the stability constants of the organotin(IV) complexes. It is found that pK_a values of the ligands in 75% dioxane-water solutions are higher than those reported in water. This may be due to the increased basicity of the ligand donor groups.

Acid-base chemistry of triphenyltin(IV) has been characterized by fitting the potentiometric data (mixture B), to various acid-base models. The fitted model was found to be consistent with a $[(Ph)_3SnOH]$ species having $\log\beta_{10\text{-}1} = -5.71$

Downloaded At: 15:30 23 January 2011

TABLE I Formation constants for triphenyltin(IV) involving amino acids and nucleotides.

system	*l*	*p*	*q*[a]	logβ[b]	*S*[c]
TPT	1	0	−1	−5.71(0.02)	1.9E-7
Glycine	0	1	1	9.74(0.02)	2.7E-10
	1	1	0	6.75(0.03)	6.4E-7
Alanine	0	1	1	9.97(0.00)	3.3E-8
	1	1	0	6.83(0.09)	9.4E-7
Proline	0	1	1	10.62(0.01)	1.8E-7
	1	1	0	7.48(0.02)	4.6E-7
Valine	0	1	1	9.75(0.00)	2.3E-8
	1	1	0	6.49(0.04)	1.1E-6
β-Phenylalanine	0	1	1	9.13(0.00)	5.0E-8
	1	1	0	6.48(0.04)	3.0E-7
S-Methylcysteine	0	1	1	9.02(0.00)	8.7E-8
	1	1	0	5.81(0.02)	3.4E-7
iso-Leucine	0	1	1	9.70(0.01)	1.2E-7
	1	1	0	6.96(0.03)	3.0E-7
Threonine	0	1	1	9.30(0.00)	3.0E-8
	1	1	0	6.22(0.02)	4.0E-7
Serine	0	1	1	9.31(0.01)	2.1E-7
	1	1	0	6.20(0.03)	6.9E-7
Methylamine	0	1	1	9.99(0.00)	2.5E-8
	1	1	0	6.73(0.01)	1.7E-7
Imidazole	0	1	1	6.02(0.01)	2.7E-8
	1	1	0	3.92(0.01)	1.1E-8
Acetic acid	0	1	1	6.92(0.00)	1.0E-9
	1	1	0	4.79(0.01)	7.2E-9
Histidine	0	1	1	9.41(0.00)	1.6E-8
	0	1	2	14.95(0.01)	
	1	1	0	6.23(0.01)	3.7E-8
	1	1	1	11.94(0.03)	
Histamine	0	1	1	9.34(0.00)	1.5E-8
	0	1	2	14.59(0.01)	
	1	1	0	5.85(0.01)	2.3E-8
	1	1	1	11.14(0.07)	
Ornithine	0	1	1	10.45(0.00)	5.6E-9
	0	1	2	19.18(0.01)	
	1	1	0	7.22(0.02)	7.1E-8
	1	1	1	16.07(0.02)	
Lysine	0	1	1	10.22(0.01)	1.3E-7
	0	1	2	19.39(0.01)	
	1	1	0	6.89(0.06)	4.8E-7
	1	1	1	16.07(0.06)	
Mercaptoethylamine	0	1	1	12.46(0.01)	2.1E-7
	0	1	2	20.82(0.01)	
	1	1	0	11.28(0.07)	4.7E-7
	1	1	1	19.70(0.06)	
Mercaptopropionic acid	0	1	1	12.37(0.01)	7.8E-8
	0	1	2	19.07(0.01)	
	1	1	0	11.89(0.07)	1.2E-7
	1	1	1	19.38(0.06)	

Downloaded At: 15:30 23 January 2011

TABLE I *cont* Formation constants for triphenyltin(IV) involving amino acids and nucleotides.

system	*l*	*p*	*q*[a]	logβ[b]	*S*[c]
Penicillamine	0	1	1	12.41(0.01)	1.2E-7
	0	1	2	20.73(0.02)	
	1	1	0	11.10(0.02)	3.1E-7
	1	1	1	18.91(0.02)	
Cysteine	0	1	1	12.24(0.01)	3.8E-7
	0	1	2	21.22(0.03)	
	1	1	0	12.98(0.09)	5.2E-7
	1	1	1	19.60(0.04)	
Inosine	0	1	1	9.41(0.01)	3.3E-8
	1	1	0	7.17(0.01)	1.5E-8
Uracil	0	1	1	10.45(0.02)	4.3E-7
	1	1	0	8.23(0.02)	2.6E-8
Thymine	0	1	1	10.93(0.01)	1.3E-7
	1	1	0	8.60(0.01)	3.6E-8
thymidine	0	1	1	11.10(0.01)	1.4E-7
	1	1	0	8.85(0.01)	3.0E-8
Adenine	0	1	1	10.80(0.02)	2.1E-7
	0	1	2	14.54(0.08)	1.7E-6
	1	1	0	6.86(0.11)	

[a]Here, l, p and q are the stoichiometric coefficients corresponding to TPT, amino acid or nucleotide, and H^+, respectively. [b]Standard deviations are given in parentheses. [c]Sum of squares of residuals.

Downloaded At: 15:30 23 January 2011

± 0.02. The concentration of the hydrolysed species increases with increasing pH, attaining a maximum of 99.9% at pH ≈ 8.6.

Potentiometric titration curves for the triphenyltin(IV)-glycine system, taken as being representative, are shown in Figure 1. The complex titration curve starts at pH ≈ 4 and is significantly lower than the ligand titration curve. This corresponds to the formation of a complex species through release of a hydrogen ion. Combined results of all ligands investigated show the formation of one complex species with a ligand-to-metal ratio of 1:1. There was no evidence for the formation of polymeric species. The stability constant, represented by the logK value, of the TPT-methylamine complex is 6.73. This is fair agreement with the stability constants obtained for the amino acids studied (Table I), if the difference in the basicity of methylamine and those of amino acids would be considered. This coincidence reveals that the amino acids coordinate to $Ph_3Sn(IV)$ as monodentates, most likely *via* the amino group. Histidine, histamine, lysine, ornithine, mercaptoethylamine, mercaptopropionic acid, penicillamine and cysteine (H_2L) form the complexes [(TPT)(L)] and [(TPT)(HL)]. The acid dissociation constant of the protonated complex is given by relationship (*3*) [15]

$$pK^{(H)}_{(TPT)(L)(H)} = \log K^{(TPT)}_{(TPT)(L)(H)} - \log K^{(TPT)}_{(TPT)(L)} \qquad (3)$$

Values of pK^H are 5.71 and 5.29 for histidine and histamine, respectively. These compare favourably with the acid dissociation constant of the imdazole residues of histidine and histamine, which are 5.54 and 5.24, respectively. Furthermore, it should be recognized that the stability constants of the deprotonated complexes of histidine and histamine are in fair agreement with the stability constants obtained for the other aminoacid complexes, but not with the imidazole complex (logK = 3.92). This provides a further support for the view that histamine and histidine coordinate to $Ph_3Sn(IV)$ through their amino groups.

Titration curves of the triphenyltin(IV) complex with mercaptopropionic acid coincide with the ligand curve in the region of neutralization of the carboxylic group. This is followed by lowering of the complex curve with respect to the ligand in the region of neutralization of the SH group. This is taken as a visual indication of complex formation through the release of a hydrogen ion from the SH group. Comparing the stability constant of the triphenyltin(IV) complex with mercaptopropionic acid (*S*-donor) and with methylamine (*N*-donor), Table I, shows that the coordination potentiality of the SH group is higher than that of the amino group.

Downloaded At: 15:30 23 January 2011

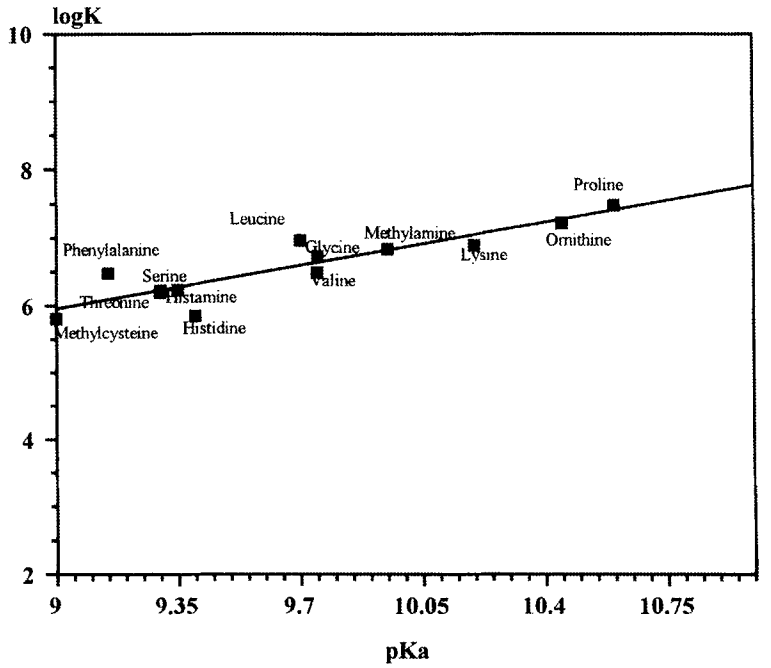


FIGURE 1 Potentiometric titration curves for the TPT-glycine system.

Penicillamine and mercaptoethylamine may coordinate either as *S*- or *N*-donors. Stability constants of their triphenyltin(IV) complexes, in the deprotonated form, are in fair agreement with that of mercaptopropionic acid (*S*-donor) and far from methylamine (*N*-donor). This reveals that penicillamine and mercaptopropionic acid bond through the *S*-atom.

The acid dissociation constant of the protonated complex formed with penicillamine calculated using (*3*) is 7.80. This compares favourably with the microscopic acid dissociation constant of NH_3^+ 8.16 [16], if the increase of acidity as a result of metal complex formation is considered.

Inosine has a dissociable proton at N_1 in the six membered ring. Both N_1 and N_7 in the imidazole ring serve as donors to metal ions in solution [17]. In the acidic pH range, N_1 remains protonated, while the metal ion is attached to N_7. The gradual change from N_7-binding to N_1-binding in complex formation with increasing pH has been extensively documented by NMR [18] and ESR [19] measurements. In the potentiometric titration of the inosine complex, the pH was varied from 5.0 to 8.80. It is therefore assumed that N_1 plays a role during complex formation. This is in agreement with Martin's conclusion [20] that starting from pH = 5-6, migration of metal ion occurs from N_7 to N_1. This is also supported by our previous investigation of Pd-DNA equilibria [21].

Uracil, thymine and thymidine have a dissociable proton at N_3. The acid dissociation constants obtained from this study were compared with that of the N_1 proton of inosine. The purinic derivative (inosine) is slightly more acidic than the pyrimidinic species (uracil, thymine and thymidine), a property which can be related to the condensed rings in inosine. Based on existing data, the pyrimidinic nucleotides bond as monoanions, most probably through the N_3 atom.

It is known that a relationship exists between the dissociation constant of a series of structurally related ligands and the stability constants of their 1:1 complexes with a given metal ion. Such a relationship can be used to estimate the stability constants of metal complexes of closely related species if their pK_a and any K_{ML} values are known. Figure 2 demonstrates such a relationship for the triphenyltin(IV) complexes of amino acids and related compounds.

Estimation of equilibrium concentrations of triphenyltin(IV) complexes as a function of pH provides a useful picture for organotin binding toward bioligands as amino acids and nucleotides. To illustrate the main features observed in the species distribution plots in these systems, the speciation diagram obtained for the triphenyltin(IV)-penicillamine system is shown in Figure 3. In all the species distributions the concentration of the complex increases with increasing pH, thus favouring complex formation with triphenyltin(IV) in the physiological pH range. Under the selected experimental conditions, the magnitude of the stability constants controls the concentration distributions of the different species.

Downloaded At: 15:30 23 January 2011

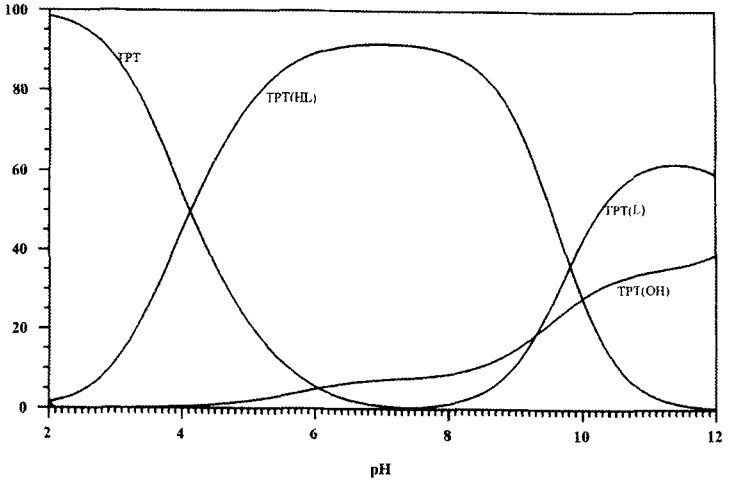


FIGURE 2 Correlation of formation constant of TPT-amino acid complex with acid dissociation constant of the amino acid.

Downloaded At: 15:30 23 January 2011

The coordination geometry of $Ph_3Sn(IV)$ is believed to be trigonal bipyramidal with three phenyl groups equatorial and two solvent molecules in axial positions, complex formation would then involve ligand substitution of one solvent molecule. The location of the two *trans* solvent molecules prevents chelation of the ligands. Similar behaviour was found for $(CH_3)_3Pb(II)$ complexes with sulfhydryl-containing amino acids [22].

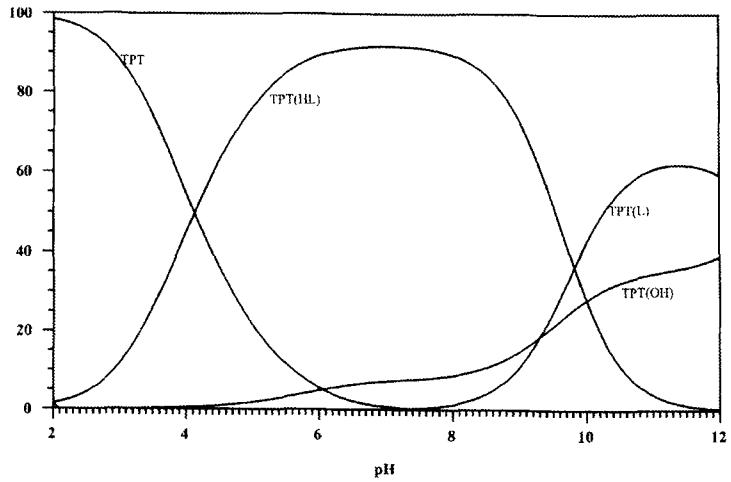


FIGURE 3 Concentration distribution of various species as a function of pH in the TPT-penicillamine system.

References

[1] G. J. M. van der Kerk and J. G. A. Luijten, *J. Appl. Chem.*, **4**, 314, (1954).
[2] M. H. Gitlitz, *Adv. Chem. Ser.*, **157**, 167, (1976).
[3] V. G. Kumar Das, *Planter (Kuala Lumpur)*, **51**, 355, (1975).
[4] Sugavanam, *Tin and Its Uses*, **126**, 4, (1980).
[5] M. M. Shoukry, *J. Inorg. Biochem.*, **48**, 271, (1992).
[6] M. M. Shoukry, *J. Coord. Chem.*, **25**, 111, (1992).
[7] M. M. Shoukry, *Bull. Soc. Chem. Fr.*, **130**, 177 (1993).
[8] M. M. Shoukry, *Talanta*, **43**, 177, (1996).
[9] R. G. Bates "Determination of pH-Theory and Practice," 2nd Edit., (Wiley Interscience, New York, 1975).
[10] M. M. Shoukry, W. M. Hosny and M. M. Khalil, *Transition Met. Chem.*, **20**, 252, (1995).
[11] R. J. Motekaitis, A. E. Martell and D. A. Nelson, *Inorg. Chem.*, **23**, 275, (1982).
[12] P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, **18**, 237, (1976).
[13] L. Pettit personal communication.
[14] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," (IUPAC, New York, 1965, 1971).
[15] M. M. Shoukry, *Talanta*, **39**, 1625, (1992).
[16] R. S. Reed and D. L. Rabenstein, *Can. J. Chem.*, **59**, 1505, (1981).
[17] R. B. Martin and Y. H. Mariam, *Metal Ions in Biol. Syst.*, **8**, 57, (1979).
[18] K. Maskos, *Acta Biochem. Pol.*, **28**, 318, (1981).
[19] K. Maskos, *J. Inorg. Biochem. Pol.*, **25**, 1, (1985).
[20] B. Noszol, V. Scheller-Krattiger and R. B. Martin, *J. Am. Chem. Soc.*, **104**, 1078, (1982).
[21] M. M. Shoukry and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 2673 (1996).
[22] S. J. Backs and D. L. Rabenstein, *Inorg. Chem.*, **20**, 410, (1980).

Downloaded At: 15:30 23 January 2011